



0883–2927(95)00002–X

Uraniferous waters of the Arkansas River valley, Colorado, U.S.A.: a function of geology and land use

R. A. Zielinski, S. Asher-Bolinder and A. L. Meier

United States Geological Survey, Denver, CO 80225, U.S.A.

(Received 10 May 1994; accepted in revised form 20 December 1994)

Abstract—The effect of local geology and land-use practices on dissolved U was investigated by analysis of surface water and some springs in the Arkansas River valley of southeastern Colorado. Water samples were collected during a 2 week period in April, 1991. The rate of increase of U concentration with distance downriver increased markedly as the river flowed from predominantly undeveloped lands underlain by igneous and metamorphic rocks to agriculturally developed lands underlain by marine shale and limestone. An additional abrupt increase in dissolved U was observed along the section of river where discharge is often greatly reduced because of extensive diversions for irrigation and where remaining flow is largely composed of irrigation return water. Dissolved U in this last section of river and in most of its tributaries exceeded the proposed U.S. drinking water standard of 20 $\mu\text{g/L}$. In water samples collected from agricultural areas dissolved U showed strong positive correlation with major dissolved constituents Na, Ca, Mg, and SO_4 that increase as a result of sulfate mineral dissolution and clay mineral ion-exchange reactions in weathered shale bedrock and shaley soils. Highly soluble minor and trace elements Cl, Li, B, Sr, and Se that are not subject to strong sorptive uptake or precipitation in this setting also correlated positively with U. These combined observations indicate that natural leaching of U-bearing shale bedrock and derivative soils, additional leaching of rock and soil by irrigation water, and evaporative concentration in a semi-arid climate can produce concentrations of dissolved U in surface water and shallow ground water that may threaten nearby drinking water supplies. Other agriculturally developed areas of the semi-arid Western U.S. with similar geology are likely to contain high concentrations of U in irrigation drain water.

INTRODUCTION

Irrigation of alkaline-saline soils in arid and semi-arid regions can contribute to the salinization of soils and of surface and ground water. The problem is particularly pronounced in areas where thin, poorly drained soils overly impermeable bedrock and where shallow water tables exist (Schwartz *et al.*, 1987). Salt-laden surface water or shallow ground water draining such soils pose additional problems because they can contain high concentrations of toxic trace elements such as Se, As, Cr, Hg, and U (Deverel and Millard, 1988; Bradford *et al.*, 1989; Feltz *et al.*, 1991).

Renewed concern regarding dissolved U in irrigation drainwater is driven by U.S. Environmental Protection Agency (USEPA) plans to implement a drinking water standard of 20 $\mu\text{g/L}$ (ppb) dissolved U by 1996 (USEPA, 1991). Enactment of this standard will produce new demands for studies of both geologic processes and land-use factors that can influence the mobility of dissolved U. We present results of one such study in the semi-arid Arkansas River valley of southeastern Colorado. This area has a long history of agricultural development and was previously documented to contain uraniferous waters (Shannon, 1978, 1979; Janzer *et al.*, 1991). Our immediate objectives were to: (1) more clearly relate the areal distribution of uraniferous waters in the river valley to geology and land use and (2) identify

the form of dissolved U and the geochemical controls on its solubility. These results can be used to predict other areas where similar geology and land use combine to produce high concentrations of dissolved U that could threaten water quality.

GEOLOGIC AND HYDROLOGIC SETTING

The study area is confined to the drainage basin of the Arkansas River in southeastern Colorado (Fig. 1). This area includes a reach of some 360 river miles (579 km) starting near Leadville, Colorado (3100 m elevation) and ending at the Colorado–Kansas border (1040 m elevation). The river initially traverses mountainous terrain underlain by Precambrian age igneous and metamorphic bedrock in the reach from Leadville to Cañon City (1650 m elevation), and then traverses flatter terrain predominantly underlain by Late Cretaceous age marine shales and limestones eastward of Cañon City (Fig. 1, modified from Tweto, 1979). The variety of bedrock lithologies in the study area confounds estimates of “typical” bedrock U concentrations. Stream sediments provide better integrated samples of bedrock materials transported from their source areas. The minus 150 micron fraction of 1800 stream sediments from the Pueblo and Lamar 2° quadrangles (Fig. 1) averages

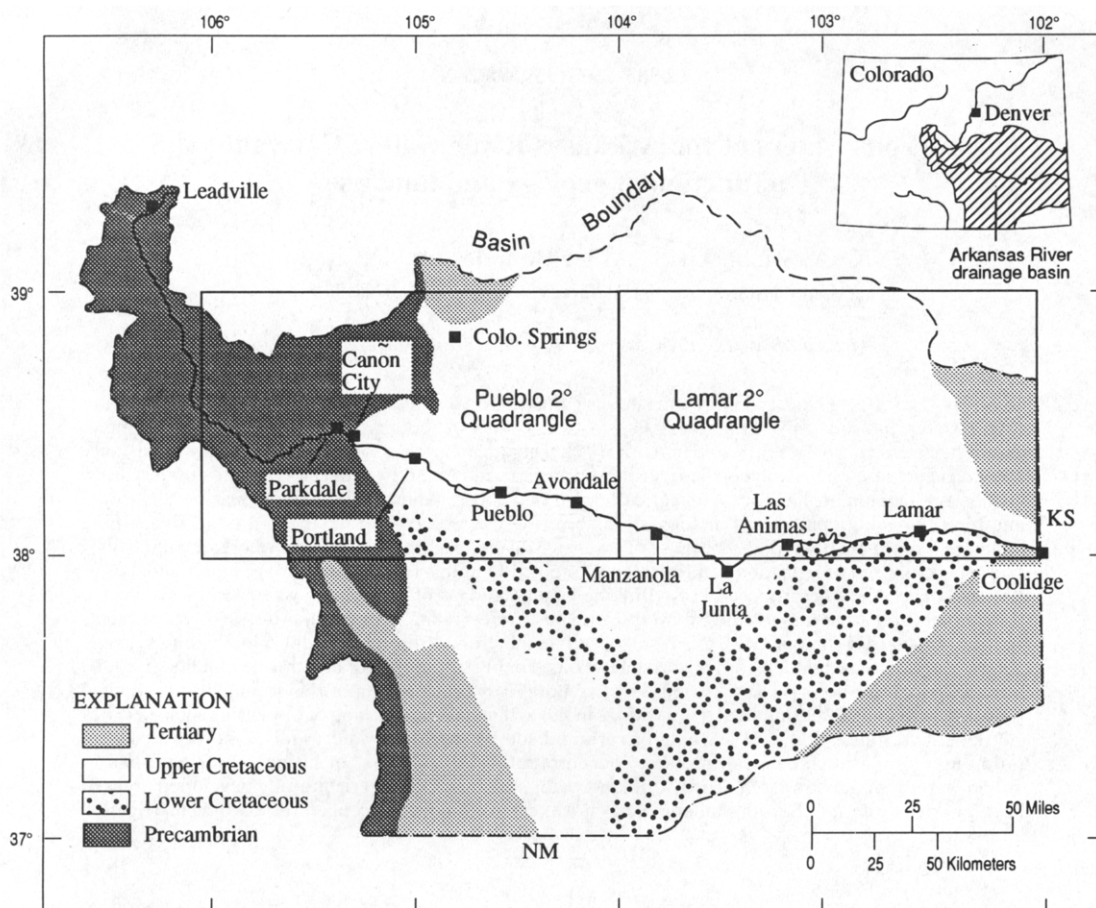


Fig. 1. Generalized geologic map of the Arkansas River basin of southeastern Colorado. The Lamar 2° and Pueblo 2° quadrangle are outlined. Modified from Tweto (1979).

$7 \pm 9 \mu\text{g/g}$ U, with a median value of approximately $5 \mu\text{g/g}$ U (Shannon, 1978, 1979).

The type and intensity of land use can be divided on a similar geographic basis. Mountainous areas are largely undeveloped but include small areas of mining activity or limited agricultural development. In contrast, the Arkansas River valley east of Cañon City has a 120-year history of intensive agricultural development. Present irrigation of approximately 160,000 ha is sustained by a complex network of irrigation canals, temporary storage reservoirs, transmountain diversions and irrigation wells (Taylor and Luckey, 1974; Abbott, 1985). Irrigated areas are mostly within 25 km of the river or adjacent to tributary streams. Open rangeland and some areas of dryland farming exist outside of irrigated areas. An area of intensive urban development is centered at Pueblo, Colorado. The study area, therefore, offers ample opportunity to investigate the effects of variable geology and land-use within a semi-arid climatic regime.

The climate of the Arkansas River basin is temperate and semi-arid. Mean daily temperature varies from -11°C (mountains in winter) to 26°C (plains in summer) and diurnal temperature variations can be

as much as 22°C . Mean annual precipitation throughout the basin ranges from 20 to 46 cm, occurring mostly as occasional thunderstorms during the spring and summer months. Limited evaporation pan data indicates that evaporation is 3.5–5 times precipitation (U.S. Department of Commerce, 1991).

Soils on the plains areas east of Cañon City originate from locally weathered (limonite-stained, gypsiferous) calcareous marine shale and limestone bedrock, or from transported mixtures of rock fragments and minerals, including some from sources in the Front Range. Most soils are calcareous and generally show some evidence of translocated soil carbonate at depth. Shale-derived soils also contain gypsum. Soils range in depth from a few cm to as much as 1.5 m, and in texture from clayey loams to sandy loams. Most soils are well-drained but finer-textured varieties have good holding capacity for residual soil moisture (Larsen *et al.*, 1972, 1979). Upland soils away from modern stream channels and floodplains are formed from residual bedrock or are derived from windblown sand and silt or old alluvial sediments, including former stream terraces and slope wash deposits (Sharps, 1976; Scott *et al.*, 1978). Soils close to modern streams are derived from recent

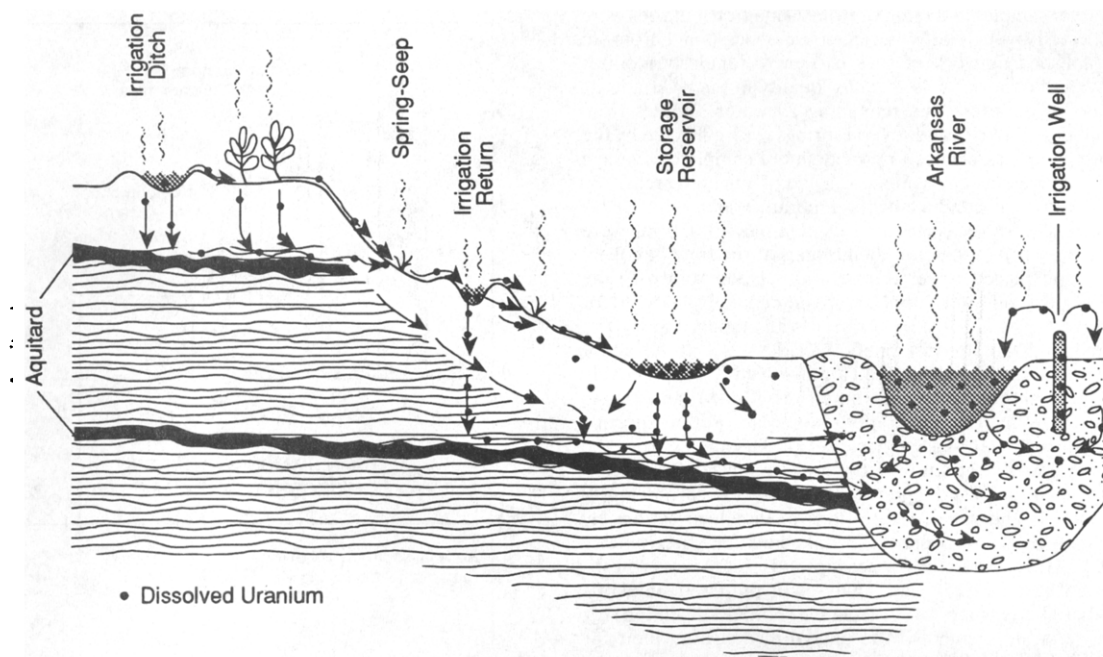


Fig. 2. Generalized summary of hydrologic pathways for irrigation water in the Arkansas River valley of southeastern Colorado.

alluvial sediments that are as thick as 15 m in tributary streams and as much as 90 m thick in the river channel (Mueller *et al.*, 1991). The U concentration of 50 shale-derived soils collected by the authors near Cañon City, Colorado (Fig. 1) ranged from 3 to 6 $\mu\text{g/g}$. Approximately 3–20 percent of this total soil-bound U was readily leachable with a mild 0.1 M solution of sodium bicarbonate (S. Asher-Bolinder, USGS, 1994, personal communication).

The hydrologic cycles of applied irrigation water are summarized in Fig. 2. One cycle begins when water is diverted from the river to surrounding lands via irrigation canals. Applied irrigation water or leakage from canals and storage reservoirs percolates through soils and enters underlying eolian or alluvial deposits that support shallow water-table aquifers developed on relatively impermeable weathered shale bedrock. Exposures of the contact between permeable sediments and bedrock are often sites of ground-water discharge in the form of springs or seeps. Based on observation of the regional topographic gradient and local measurements of water table contours, much of this shallow ground water eventually returns to the alluvial aquifer of the river (Konikow and Bredehoeft, 1974; Cain, 1980). This ground-water return may be direct or via alluvial aquifers of the many tributary streams. If returning ground water enters the alluvial aquifer of the river, it may be subject to a second important cycling that involves pumpage from irrigation wells, infiltration and recharge to the aquifer, and repeated pumpage from wells downriver. In addition to ground-water return, returns of irrigation runoff occur via tributary

streams and a network of constructed return drains. Returns of this runoff and of shallow ground water that help sustain surface flow in the river are available for repeated diversion in downstream canals. Recycling of irrigation water promotes enhanced water/soil and water/rock interactions that contribute to progressive downriver increases in total dissolved solids in both surface and ground water (Konikow and Person, 1985; Cain, 1987). At all stages of these cycles when waters are at or within approximately 3 m of the surface they are subject to additional concentration through evaporation. Depth to water in the shallow water-table aquifers ranges from land surface to approximately 30 m, with typical depths less than 9 m (Cain, 1980).

SAMPLE COLLECTION AND ANALYSIS

A total of 77 surface water and spring samples were collected during a 2 week period in mid-April 1991. Natural flows in April are representative of the early spring season and are a location-dependent mixture of ground-water seepage and very early spring runoff. In irrigated areas these natural flows are further affected by releases from storage reservoirs, diversions to irrigation canals, and return flow from early stages of irrigation. These waters, collected under moderate-flow, largely prerunoff conditions, provide a relatively instantaneous snapshot of downriver changes in dissolved U with respect to changes in surrounding geology and land use. River and stream discharges at this time of year are more typical of the norm than are discharges during the spring runoff period in May–July (U.S. Geological Survey, 1991). Sampling sites included 19 locations along the Arkansas River from Leadville to Lamar, and the mouth of most of the tributary streams. The

19 river samples and samples from 29 major tributaries were collected by USGS Water Resources personnel from an established network of sites chosen to regularly monitor flow and other aspects of water quality in the river and its major tributaries. The remaining 29 water samples from smaller tributaries and several springs were collected by the authors and associates to provide more complete coverage and to include some samples outside of irrigated areas.

The specific conductance, temperature and pH of water samples were measured *in situ*. Samples of 250 ml were filtered through 0.45 μm membranes at the time of collection and placed under refrigeration. Upon return to the laboratory all water samples were immediately analyzed for alkalinity (as HCO_3^-) by titration with standard acid. The remaining sample was acidified to $\text{pH} < 2$ with ultrapure grade nitric acid and analyzed for dissolved U by inductively coupled plasma-mass spectrometry (ICP-MS), and for As and Se by hydride generation-atomic absorption spectrophotometry (HGAAS). A subset of 39 samples from the eastern part of the study area was also analyzed for concentrations of dissolved anions (Cl , SO_4) by ion chromatography (IC), and for concentrations of dissolved cations by inductively coupled plasma-atomic emission spectrometry (ICP-AES). Analytical precision and accuracy were estimated based on replicate analyses of prepared standards and are better than $\pm 10\%$ (relative standard deviation) for the reported elements. The analytical detection limit for dissolved U was 0.1 $\mu\text{g/L}$.

RESULTS AND DISCUSSION

Reexamination of existing data

The National Uranium Resource Evaluation (NURE) Program of the middle 1970s identified eastern Colorado as an area with consistently high concentrations of dissolved U in surface and ground water. For example, the mean U concentration in ground water in the Lamar 2° quadrangle of south-eastern Colorado (Fig. 1) is 19.4 $\mu\text{g/L}$ —a concentration two to four times that of ground water in most other NURE quadrangles in the Western U.S. (Shannon, 1979). Almost the entire Lamar quadrangle is underlain by Upper Cretaceous marine shale and limestone of the Pierre Shale and Niobrara Formation (Fig. 1), but marked differences in land use exist in different parts of the quadrangle. The southern quarter includes the Arkansas River valley and all the irrigated lands adjacent to the river, whereas the rest of the quadrangle consists of largely undeveloped rangeland. The NURE data were re-examined with regard to location within the Lamar quadrangle and it was found that well waters from the southern quarter have markedly higher median U concentration (15 $\mu\text{g/L}$) than well waters in the rest of the quadrangle (10 $\mu\text{g/L}$) (Fig. 3). Both frequency distributions illustrate large degrees of dispersion. The frequency distribution from the southern quarter is skewed towards higher values and therefore has a higher median value. Nonparametric tests of the differences between population medians indicated that differences are statistically significant at the $>95\%$ confidence level.

The NURE data also suggests that differences in

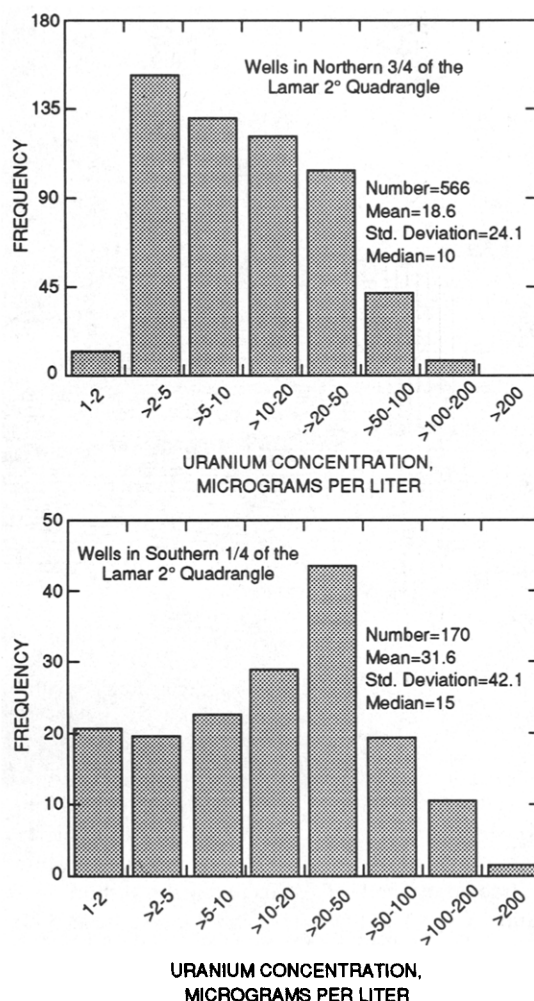


Fig. 3. Frequency distributions of U concentration in well waters from different parts of the Lamar quadrangle, Colorado. Data are limited to wells (90%) containing greater than 1 $\mu\text{g/L}$ U. Well depths are often unspecified but most of the reported well depths are <46 m. Data recast from Shannon (1979).

dissolved U are related to bedrock geology. Data for 75 springs in Precambrian crystalline rock collected in the western half of the Pueblo 2° quadrangle west of Cañon City average 9.9 ± 22 $\mu\text{g/L}$ U (Shannon, 1978). This value is low compared to our estimated average of approximately 18 $\mu\text{g/L}$ U for ground water in contact with Cretaceous bedrock units in the undeveloped northern 3/4 of the Lamar quadrangle.

The above comparisons are based on the results of areally extensive sampling of broadly defined water types conducted over many weeks. A more spatially and temporally focused investigation of the effects of both geology and land use on dissolved U is discussed below.

Distribution of U in waters sampled in April, 1991

Sample locations and U-concentration data for the samples of this study are summarized in Fig. 4.

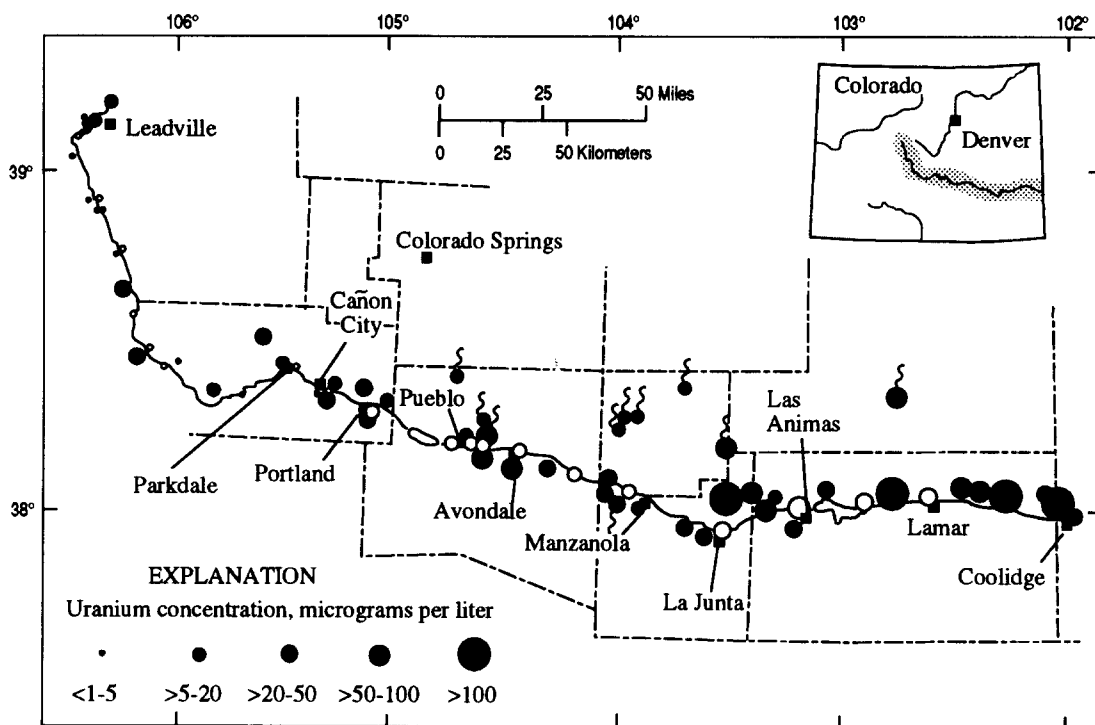


Fig. 4. Location of surface water and spring samples collected in this study. Sample locations are codified according to the U concentration measured in the water. Tributary samples are shown as closed circles, river samples as open circles. Spring samples are identified by a circle with a tail.

Coding of the sample sites according to dissolved U concentration clearly illustrates the general trend of increasing downriver concentrations in both the Arkansas River and its tributary streams (Fig. 4). Dissolved U in the main stem of the Arkansas River ranges from $<1\text{--}50\text{ }\mu\text{g/L}$ (Fig. 5). This compares to a recently reported average concentration of $0.3\text{ }\mu\text{g/L}$

U for 40 major rivers of the world (Palmer and Edmond, 1993). These results are discussed by considering three distinct sections of the river.

In the uppermost section from Leadville to Cañon City, dissolved U in the Arkansas River gradually increased from less than 1 to $3.3\text{ }\mu\text{g/L}$. Low U concentrations in snowmelt-derived water are not greatly modified through contact with predominantly igneous and metamorphic bedrock and alluvium over 120 river miles (193 km). Some slightly elevated U concentrations in tributaries ($5\text{--}20\text{ }\mu\text{g/L}$) can be attributed to the influence of acidic mine drainage near Leadville and to drainage from volcanic and volcanoclastic rocks that host some U mines northwest of Parkdale. None of these local tributaries supplied enough dissolved U to dramatically “spike” dissolved U in nearby sampling sites along the Arkansas River.

In the 100-mile-long (160 km) middle reach from Cañon City to Manzanola, dissolved U in the river again increased regularly from 3.3 to $14\text{ }\mu\text{g/L}$, but at a faster rate (Fig. 5). Tributaries and a few sampled springs contain moderate U concentrations ($5\text{--}50\text{ }\mu\text{g/L}$). We propose that generally higher U concentrations in tributaries and more rapidly rising U concentrations in the Arkansas River reflect the transition to (1) Upper Cretaceous marine shale and limestone bedrock and (2) the beginning of irrigation practices (approximately 30% of the irrigated acreage along the Arkansas River valley borders this section of river). Our set of river sampling sites

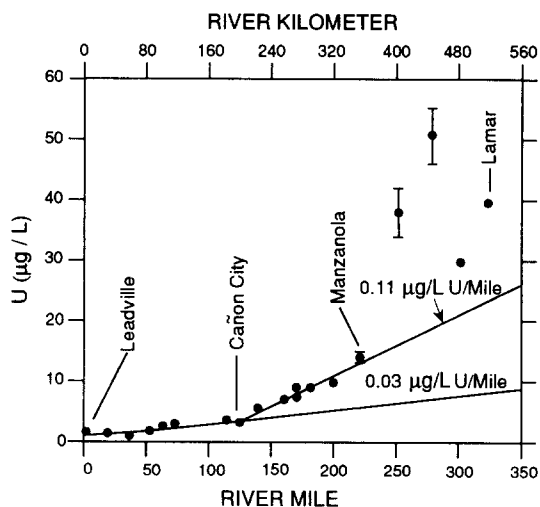


Fig. 5. Uranium in Arkansas River water, April, 1991, plotted as a function of river mile (and river km) from Leadville, Colorado. Visually fitted linear trends labeled (a) and (b) define different rates of increase of dissolved U concentration in two sections of river with contrasting geology and land use.

showed no particular spike of dissolved U from a former U extraction mill near Cañon City or from urban development near the town of Pueblo.

In the lower section of river from Manzanola to Lamar, the dissolved U concentration does not increase in a linear fashion, and concentrations scatter within the 30 to 50 $\mu\text{g/L}$ range. All the values plot well above the linear trend defined by the rate of increase of dissolved U in the middle section of river (Fig. 5). Tributary and spring U concentrations are in the 20 to 100 $\mu\text{g/L}$ range with some concentrations exceeding 100 $\mu\text{g/L}$ (Fig. 4). This section of river is distinguished from the middle section by markedly decreased mean annual discharge (10–40% of that at Manzanola), and increased contribution of recycled irrigation-return waters to total discharge (Cain, 1985). For the month of April, 1991 mean discharge at Manzanola was 7.5 m^3/s compared to <1.4 m^3/s at gaging stations in La Junta, Las Animas, and Lamar (U.S. Geological Survey, 1991). The local adage that “the Arkansas River ends at Manzanola” is based on the fact that water diversions create a near zero-flow condition during parts of the irrigation season. Below Manzanola a much greater percent of discharge is either directly delivered drain water or irrigation return indirectly delivered through tributaries and groundwater seepage. Groundwater recharged to the alluvial aquifer is further cycled to the surface by pumping from over 1000 irrigation wells (Taylor and Luckey, 1974). It is proposed that surface waters sampled along this section of river and in adjoining tributaries are enriched in dissolved U and other constituents by virtue of their extensive use and reuse during irrigation. It is further proposed that the amount of additional enrichment of U in river water can be estimated by comparing measured concentrations to those predicted by the upper trend line of Fig. 5. The upper trend line is based on the rate of U increase along the middle section of river that traverses similar rock types but supports less irrigation and is much less affected by irrigation-water return.

Aqueous geochemistry of U

Dissolved U in all 49 samples collected east of Cañon City shows a strong positive correlation ($r = 0.82$) with specific conductance indicating that dissolved U is soluble and conserved in solution. This relation, which is commonly observed in natural waters, suggests that the more easily measured property of specific conductance may be used to estimate the potential of high U concentration in water from the study area. Previous studies of the temporal and spatial variability of specific conductance in the Arkansas River valley (Konikow and Person, 1985; Cain, 1987) may therefore suggest patterns of historic variability of dissolved U.

Summary statistics for 18 measured variables in the 39 river and tributary samples collected east of Cañon

City are presented in Table 1. As with the larger population of samples that also includes springs, there is a positive correlation between U and specific conductance ($r = 0.84$). Uranium correlates positively ($r > 0.69$) with the major dissolved species Na, Ca, Mg, SO_4 , and Cl that strongly contribute to specific conductance. Also showing strong positive correlation with U ($r > 0.78$) are the minor elements Li and Sr that have geochemical affinity with the major dissolved species, and B and Se that commonly concentrate in oxic saline waters of the Western U.S. Plots illustrating the correlation of U with some of these constituents are presented in Fig. 6.

A less well-defined correlation exists between U and pH, which rarely shows strong covariation with specific conductance in natural waters, and between U and dissolved bicarbonate, silica and manganese, which are probably limited by solubility of the observed phases calcite, secondary silica, and secondary Mn oxides. Smaller subsets of samples containing measurable Fe and Ba also show poor correlation with U, again suggesting solubility control, probably through precipitation of secondary Fe oxides (observed) and barite. Poor correlation of Fe (and Mn) with dissolved U can also be attributed to their contrasting solubility as a function of Eh.

The extent of saturation of Arkansas River waters with minerals proposed to influence dissolved U and other aspects of water chemistry was investigated by equilibrium-based, mineral-solubility calculations using the computer code PHREEQE (Parkhurst *et al.*, 1980). The thermodynamic database for dissolved U species and U minerals was from Langmuir, 1978. For the purpose of the calculations an oxidizing Eh of 0.4 V was assumed for these oxygenated surface waters. Figure 7 presents results for 8 Arkansas River waters (Table 2) collected at increasing distances downstream from Parkdale, just west of Cañon City. All samples are saturated, or very nearly saturated with calcite, dolomite, quartz, ferric hydroxide, and barite (not shown). In contrast, the same waters are undersaturated in amorphous silica, gypsum, and mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$), the latter chosen as an analog for the variety of white, highly soluble Na, (Na, Mg) and (Na, Ca)-sulfate salts that form as efflorescent crusts on soils of the area. The sulfate minerals show increasing approach to saturation as the water chemistry evolves from a low total dissolved solids (TDS), Ca–Mg– HCO_3 chemistry at the mountain front to a high TDS, Mg–Ca–Na– SO_4 chemistry after contact with shale-derived soils and shale bedrock. Ground water that shows this type of chemical evolution is commonly modeled by a combination of gypsum dissolution and Ca–Na ion exchange (Fisher and Mullican, 1990). In the case of these surface waters additional controls include the variable effects of evaporative concentration and dissolution of efflorescent salts.

All eight river waters were greatly undersaturated with respect to oxidized U minerals, as illustrated in

Table 1. Statistical summary of chemical data for 39 surface-water samples from the Arkansas River valley east of Cañon City, Colorado, collected April, 1991

Variable	<i>n</i>	Minimum	Maximum	Median	Mean	Standard deviation	Correlation coefficient with U
Sp. Cond. ($\mu\text{S}/\text{cm}$)	39	229	8000	2290	2681	1983	0.84
pH	39	7.55	8.70	8.10	8.09	0.25	-0.37
Major elements (mg/l)							
SiO ₂	39	1.3	34	14	15	6.9	0.31
Sodium	39	9.0	1000	150	259	265	0.86
Potassium	39	1.0	36	5.0	6.9	6.8	0.50
Calcium	39	26	580	245	240	147	0.70
Magnesium	39	7.0	490	94	119	111	0.77
Bicarbonate	39	95	625	280	283	102	0.30
Sulfate	39	28	5080	1016	1344	1250	0.82
Chloride	39	1.7	320	37	70.6	85.3	0.87
Minor elements* ($\mu\text{g}/\text{l}$)							
Boron	34	<100	2000	260	394†	404†	0.96†
Lithium	39	28	540	95	129	124	0.87
Manganese	28	<20	620	36	75.3†	127†	0.06†
Selenium	35	<1	68	12	14.9†	13.0†	0.79†
Strontium	39	220	11000	4100	4335	3195	0.79
Uranium	39	3.3	220	34	45	47	1.00
Less frequently detected elements ($\mu\text{g}/\text{l}$)							
Σ Diss. iron	13	<50	200	—	—	—	-0.22
Barium	22	<40	870	—	—	—	-0.19

n, number of values above detection. Sp. Cond. ($\mu\text{S}/\text{cm}$), specific conductance (microsiemens per centimeter at 25°C); SiO₂, silicon dioxide; U, uranium; dashes indicate value not calculated.

*Other elements sought but consistently below detection limit ($\mu\text{g}/\text{l}$) include; silver(2), arsenic(2), beryllium(1), bismuth(10), cadmium(1), cobalt(3), chromium(1), copper(10), gallium(5), molybdenum(10), nickel(5), lead(10), tin(10), vanadium(6), zinc(3), and zirconium(1).

†Calculated after assigning a value of 0.7 of the detection limit to undetected samples.

Fig. 7 by calculations for some of the relatively insoluble uranyl vanadates, carnotite, and tyuyamunite. For these calculations a maximum of 6 $\mu\text{g}/\text{L}$ V was chosen, based on the detection limit value. Precipitation of U as reduced U^{IV} minerals is calculated to be possible at Eh < 0.1 V, but such reducing conditions are unlikely to persist in organic-poor surface environments or in shallow unconfined aquifers that are open to exchange with the atmosphere and that contain sparse fresh organic matter. In fact the generally high concentrations of dissolved U and its apparent conservative behavior in solution indicate that, in this setting, solution transport of U dominates over sorptive uptake or precipitation under reducing conditions. To assess the importance of U fixation in reducing environments we collected 39 auger samples of organic-rich soils at 8 sites. These sites included spring mouth (*n* = 3), lake margin (*n* = 1), stream margin (*n* = 1), and slough (*n* = 3) and all had high concentrations of dissolved U in associated surface water or spring water. As further evidence of probable reducing conditions at these sites, the activity of sulfate-reducing bacteria produced associated black precipitates of suspected iron monosulfides. The U concentration we observed in these soils was only moderately elevated (4–15 $\mu\text{g}/\text{g}$) compared to 3–6 $\mu\text{g}/\text{g}$ in typical shaley soils.

High solubility of U is expected in oxygenated

alkaline-pH surface waters if they contain sufficient concentrations of dissolved carbonate to stabilize U as uranyl carbonate complexes (Langmuir, 1978). Calculations of U speciation with PHREEQE indicated that uranyl di- and tri-carbonate complexes account for more than 95% of the inorganic U species in the nine river waters. Uranyl phosphate complexes are also very stable but are not significant in waters of pH > 7.2 and low to medium ionic strength (Grenthe *et al.*, 1992). In this study uranyl phosphate complexes were calculated to be very minor (<5%) components of U species in typical Arkansas River waters that contain <0.1 mg/L dissolved orthophosphate (Gaydos, 1980; Cain, 1985).

The possible existence of macromolecular uranyl-organic complexes or of U-containing colloids is not addressed by the computer code, but was investigated by a size-exclusion technique utilizing a dialysis membrane. Ten milliliters of 0.45 μm filtered, unacidified river water were sealed inside a length of dialysis tubing of nominal molecular weight cutoff equal to 1000 (Spectra/Por 7). Each of four samples (Parkdale, Avondale, La Junta, Lamar) was dialyzed against 3 L of distilled deionized water at pH = 6–7 for 48 h. The dialyzed samples, which had final conductances of <50 $\mu\text{S}/\text{cm}$ were re-analyzed for U. Uranium that remained inside the tubing was assumed to be associated with retained macromol-

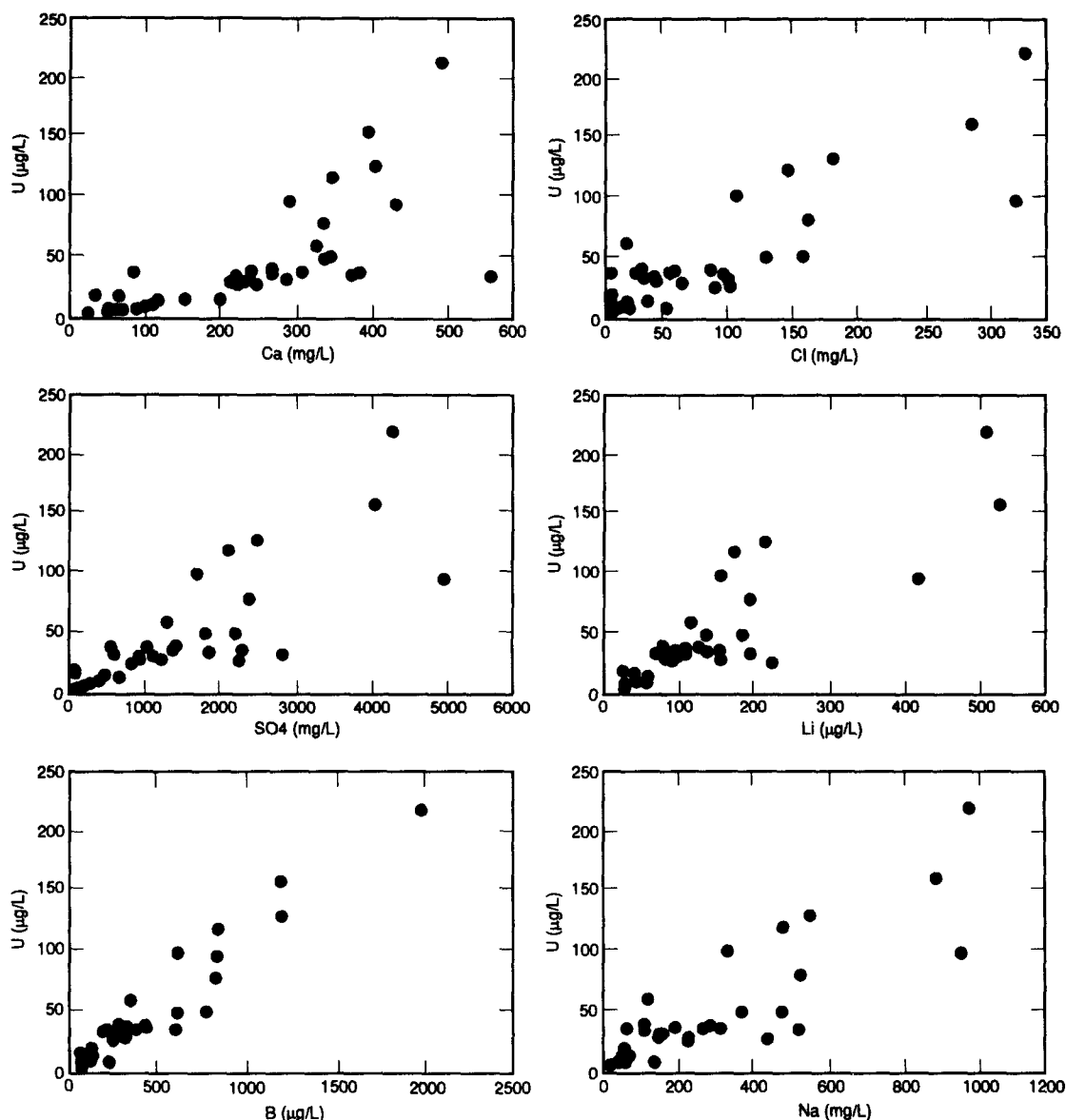


Fig. 6. Correlation plots of dissolved U versus other dissolved constituents in 39 water samples collected from the Arkansas River and its tributary streams, east of Cañon City, Colorado.

ecules of organic matter (e.g. humic acids) or colloids of >1000 molecular weight. Results indicated that the fraction of retained U was small in all four samples and decreased from 5.5% in the Parkdale sample to 1.7% in the most uraniferous sample from Lamar. These limited results indicate that most of the U is present as truly dissolved species or as a complex with very small organic molecules (fulvic acids?).

Our data for another toxic trace element Se (Table 1) support the findings of Mueller *et al.* (1991) who reported concentrations in surface and ground water along the Arkansas River valley of Colorado that exceeded the then operative USEPA drinking water standard of $10 \mu\text{g/L}$. Selenium concentrations reported in this study do not exceed the present drinking water standard of $50 \mu\text{g/L}$ (USEPA, 1993).

Likewise, concentrations of the other measured toxic trace elements As, Ba, Be, Cd, Cr, Ni, and Pb (Table 1) do not exceed present USEPA drinking water standards (USEPA, 1993).

ENVIRONMENTAL IMPLICATIONS

This study indicates that irrigation in southeastern Colorado has raised naturally high dissolved U concentrations in surface water and shallow ground water to levels that can exceed the proposed USEPA drinking water standard. Dissolved U is therefore an additional water-quality concern for the local population, and U analysis of unregulated private wells and regulated municipal water systems is recom-

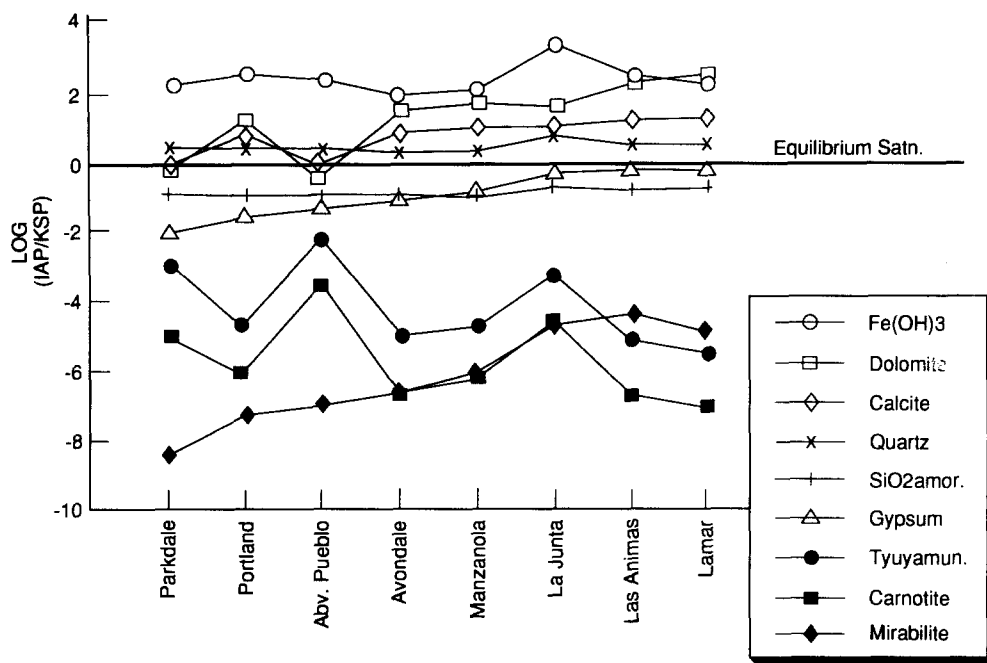


Fig. 7. Calculated saturation indices of selected mineral phases in nine samples of Arkansas River water collected at progressive distances downstream from Parkdale, Colorado. Calculations for two uranyl vanadate minerals are upper limits based on detection-limit abundances of vanadium of $6 \mu\text{g/L}$.

mended. Of particular concern are public water systems in extreme southeastern Colorado that utilize shallow spring water or water from the alluvial aquifer. Remediation by treatment of individual water supplies is the most practical solution because it is not clear that modification of land use or irrigation practices will produce a timely or satisfactory

reduction in dissolved U. This is largely because the estimated concentration of $18 \mu\text{g/L}$ U for average natural background concentration is close to the proposed regulatory limit of $20 \mu\text{g/L}$.

Other nearby irrigated areas with similar geology, climate and land use that have high dissolved U in surface or ground water include the Platte River

Table 2. Chemistry of Arkansas River water collected at progressive distances downstream from the Cañon City area, southeastern Colorado. Samples collected April, 1991

	Parkdale	Portland	Above Pueblo	Avondale	Manzanola	La Junta	Las Animas	Lamar
Major chemical species ($\mu\text{g/l}$)								
SiO ₂	8.6	8.6	8.6	8.6	8.6	17.1	12.9	15.0
Na	9.0	27	27	52	76	200	380	290
K	1	2	3	4	4	5	6	7
Ca	26	51	63	86	120	280	350	350
Mg	20	17	20	29	43	100	140	130
Fe (Σ diss.)	<0.05	0.07	<0.05	<0.05	<0.05	0.2	0.09	0.1
HCO ₃	95	140	160	185	220	323	363	345
SO ₄	74	120	168	300	430	1090	1830	1440
Cl	2.9	5.5	3.1	10	15	52	125	81
Temp ($^{\circ}\text{C}$)	11.5	11.0	8.5	16.0	13.0	7.5	14.5	18.0
Sp. Cond. ($\mu\text{S/cm}$)	230	490	575	850	1210	2580	3760	3350
pH	8.1	8.7	7.7	8.4	8.4	8.1	8.2	8.2
Minor and trace chemical species ($\mu\text{g/l}$)								
As	<2	<2	<2	<2	3	<2	<2	<2
B	<100	<100	<100	110	130	330	610	420
Ba	87	51	61	53	49	64	44	40
Li	41	<40	<40	<40	44	110	140	130
Mn	39	37	<20	<20	25	80	260	43
Se	<1	<1	3	10	11	18	13	11
Sr	800	560	770	1100	1600	5200	6500	4800
U	3.6	5.6	7.2	9.0	14	38	51	40

Abbreviations and detection limits for other trace elements sought but not found are the same as for Table 1.

valley of northeastern Colorado (Boberg and Runnells, 1971), and the Arkansas River valley of western Kansas (U.S. Department of Energy, 1980). On a regional scale, irrigated lands of the semi-arid Western U.S. that are underlain by weathered marine shales should be investigated. This includes parts of agriculturally developed lands in the northern Great Plains, Colorado-Utah, and California, and includes many of the areas targeted for possible elevated dissolved Se (Feltz *et al.*, 1991). The Arkansas River valley of Colorado or the San Joaquin valley of California (Pradford *et al.*, 1989) may be among the most affected areas because they have an abundant supply of water and a long history of intensive agricultural development. As areas with uraniferous surface water and ground water are identified they should be further assessed according to the degree of hydrologic connection between U-contaminated water and local drinking water sources.

The eventual fate of U that leaves Colorado in the Arkansas River is also an issue of concern. With progressive eastward transport towards the Mississippi River dissolved U is subject to dilution with tributary discharge from areas that receive more rainfall and are underlain by other bedrock lithologies. In addition the more humid climate of the Midwest supports organic-rich riparian zones that can provide sites for U sorption. When considering the overall effect of change to a humid climatic regime, increased rainfall coupled with generally more organic-rich, acid soils, combine to reduce dissolved U concentrations and destabilize uranyl carbonate complexes. Thus, areally extensive contamination of water with U derived from irrigation of shaley soils/bedrock probably is limited to arid and semi-arid regions.

High concentrations of dissolved U in irrigation water suggests a potential for increased concentration of U in food crops, but the magnitude of this effect is difficult to predict because of independent variation of other factors that can influence U uptake such as U concentration in soils, soil conditions, pore water chemistry and crop type (Mortvedt, 1994). Limited data for plant/soil concentration ratios (CR) indicate that plant uptake of U is highly variable but is also highly inefficient ($CR \ll 1$) for crops grown on natural soils (Mortvedt, 1994). The combination of low U contents (0.01–0.1 $\mu\text{g/g}$) in most food (Cothorn *et al.*, 1983) and low fractional absorption (0.005–0.05) of U across the gastrointestinal tract into the blood of humans (Linsalata, 1994) makes drinking water the major source of U intake. The radiotoxicity of ingested U is unknown but limited clinical studies suggest that U is chemically toxic, particularly to the kidneys (Cothorn *et al.*, 1983).

A final point of environmental concern is the possible impact of fertilizer application. Phosphate-bearing fertilizers contain U that originates from phosphate rock and this U may also be available for dissolution in irrigation drainage. Samples of seven

phosphate-bearing fertilizers applied in the study area contained 35–150 $\mu\text{g/g}$ U. Phosphate-bearing fertilizer is widely applied in the fall or very early spring to alfalfa, corn and other vegetable crops grown throughout the valley. Widespread application of phosphate fertilizer limits the ability to distinguish between leached natural U and fertilizer U because observations are based on the spatial distribution of uraniferous waters. Boberg and Runnells (1971) used mass balance arguments to discount the effect of fertilizer U in the South Platte river valley. More direct evidence is based on an ongoing study along one of the smaller tributary streams of the Arkansas River near Avondale, Colorado (Fig. 1). Preliminary results using U isotopes to identify U sources indicate that the dissolved U is of soil and bedrock origin.

CONCLUSIONS

In semi-arid southeastern Colorado, natural oxidative weathering of U-bearing marine shale bedrock, leaching of shale-derived soils, and evaporative concentration produces average U concentrations in surface water and shallow ground water that approach and exceed the proposed USEPA drinking water standard of 20 $\mu\text{g/L}$. Locally extensive use and reuse of water during irrigation of the Arkansas River valley further elevates dissolved U concentrations in irrigation return waters by increasing the amount of water/soil and water/rock interaction, and the potential for evaporative concentration.

Dissolved U occurs in these oxygenated waters as stable uranyl carbonate complexes that hinder sorptive uptake of U by coexisting solids. Our limited data suggest that transport of U as colloids is very minor in Arkansas River waters. Dissolved U correlates positively with other major (Na, Mg, SO_4 , Cl) and minor (Li, K, B, Sr, Se) dissolved species that are not limited by major sorptive uptake or the solubility of mineral precipitates. In this setting, specific conductance serves as an easily measured, albeit approximate, predictor of dissolved U concentration.

In sparsely populated areas like southeastern Colorado with high natural backgrounds of dissolved U, treatment of individual water supplies to remove U is more practical than modification of irrigation practices. Any efforts to remediate high concentrations of dissolved U must however, be integrated with existing plans to address local water quality problems. For example, a combination of water treatment and modified irrigation practices may better address water quality problems in areas where waters contain both high dissolved U and total dissolved solids.

Other areas of the arid and semi-arid Western U.S., where saline-alkaline soils overlie weathered marine shale bedrock, and where shallow water tables are developed, are predicted to contain natur-

ally uraniferous surface water and shallow ground water. This includes parts of the northern Great Plains, Colorado, Utah and California. Extensive irrigation of such areas can produce concentrations of dissolved U in irrigation drain waters that may threaten local water supplies.

Acknowledgements—Special thanks to D. L. Cain, P. F. Edelman, and R. F. Ortiz of the USGS Water Resources Division, Pueblo subdistrict for providing helpful discussions and background information on water quality and usage in the Arkansas River valley, and for providing water samples. P. L. Sutherland of the U.S. Department of Agriculture provided helpful information on local soils and the history of irrigation and agriculture in southeastern Colorado. J. K. Otton and D. L. Owen of the USGS provided critical assistance in water sampling and soil sampling. Other USGS personnel who provided analytical support included P. H. Briggs, R. J. Knight, M. J. Malcolm, G. O. Riddle, R. B. Vaughn, R. B. Wanty, and E. P. Welsch.

Editorial handling: Ron Fuge.

REFERENCES

- Abbott P. O. (1985) Description of water systems operations in the Arkansas River basin, Colorado. *U.S. Geol. Surv. Water-Res. Invest. Rep.* 85-4092.
- Boberg W. W. and Runnells D. D. (1971) Reconnaissance study of uranium in the South Platte river, Colorado. *Econ. Geol.* **66**, 435–450.
- Bradford G. R., Bakhtar D. and Westcot D. (1989) Uranium, vanadium, and molybdenum in saline waters of California. *J. Envir. Qual.* **19**, 105–108.
- Cain D. (1980) Hydrogeology and chemical quality of ground water in Crowley county, Colorado. *U.S. Geol. Surv. Water-Res. Invest. Open-File Rep.* 80-681.
- Cain D. (1985) Quality of the Arkansas River and irrigation-return flows in the lower Arkansas River valley, Colorado. *U.S. Geol. Surv. Water-Res. Invest. Rep.* 84-4273.
- Cain D. (1987) Relations of specific conductance to stream-flow and selected water-quality characteristics of the Arkansas River basin, Colorado. *U.S. Geol. Surv. Water-Res. Invest. Rep.* 87-4041.
- Cothern C. R., Lappenbush W. L. and Cotruvo J. A. (1983) Health effects guidance for uranium in drinking water. *Health Phys.* **44**, 377–384.
- Deverel S. J. and Millard S. P. (1988) Distribution and mobility of selenium and other trace elements in shallow groundwater of the western San Joaquin Valley, California. *Environ. Sci. Technol.* **22**, 697–702.
- Feltz H. R., Sylvester M. A. and Engberg R. A. (1991) Reconnaissance investigations of the effects of irrigation drainage on water quality, bottom sediment, and biota in the Western United States. In *U.S. Geological Survey Toxic Substances Hydrology Program*, Proceedings of the technical meeting, Monterey, California, March 11–15, 1991 (eds G. E. Millard and D. A. Aronson), pp. 319–323. *U.S. Geol. Surv. Water-Res. Invest. Rep.* 91-4034.
- Fisher R. S. and Mullican W. F. III (1990) *Integration of ground-water and vadose-zone geochemistry to investigate hydrochemical evolution: a case study in arid lands of the northern Chihuahuan desert, Trans-Pecos, Texas*. Texas Bureau of Economic Geology, Geological Circular 90-5.
- Gaydos M. W. (1980) Summary of water quality data for selected streams in Colorado. *U.S. Geol. Surv. Water-Res. Invest. Rep.* 80-682.
- Grenthe I., Fuger J., Lemire R. J., Mueller A. B., Nguyen-Trunge C. and Wanner H. (1992) *Chemical thermodynamics of uranium*. NEA-OECD, North Holland.
- Janzer V. J., Stanley G. W., Long H. K., Farrar J. W. and Brezina K. A. (1991) Data for gross alpha, gross beta, gross radium as radium-226, and uranium in ground and surface waters in the United States, mid-1954 through 1965. *U.S. Geol. Surv. Open-File Rep.* 91-70.
- Konikow L. F. and Bredehoeft J. D. (1974) Modelling flow and chemical quality changes in an irrigated stream-aquifer system. *Water Resour. Res.* **10**, 546–562.
- Konikow L. F. and Person M. (1985) Assessment of long-term salinity changes in an irrigated stream-aquifer system. *Water Resour. Res.* **21**, 1611–1624.
- Langmuir D. (1978) Uranium solution-mineral equilibria at low temperatures with application to sedimentary ore deposits. *Geochim. cosmochim. Acta* **42**, 547–569.
- Larsen R. J., Martin D. R. and McCullough M. B. (1972) *Soil survey of Otero County, Colorado*. U.S. Dept. of Agriculture, Soil Conservation Service.
- Larsen R. J., Wiggins T. J., Holden D. L., McCulloch M. B. and Preator R. E. (1979) *Soil survey of Pueblo area, Colorado; parts of Pueblo and Custer Counties*. U.S. Dept. of Agriculture, Soil Conservation Service.
- Linsalata P. (1994) Uranium and thorium decay series radionuclides in human and animal foodchains—a review. *J. Environ. Qual.* **23**, 633–642.
- Mortvedt J. J. (1994) Plant and soil relationships of uranium and thorium decay series radionuclides—a review. *J. Environ. Qual.* **23**, 643–650.
- Mueller D. K., DeWeese L. R., Garner A. J. and Spruill T. B. (1991) Reconnaissance investigation of water quality, bottom sediment, and biota associated with irrigation drainage in the middle Arkansas River basin, Colorado and Kansas, 1988. *U.S. Geol. Surv. Water-Res. Invest. Rep.* 91-4060.
- Palmer M. R. and Edmond J. M. (1993) Uranium in river water. *Geochim. cosmochim. Acta* **57**, 4947–4955.
- Parkhurst D. L., Thorstenson D. C. and Plummer L. N. (1980) PHREEQE—A computer program for geochemical calculations. *U.S. Geol. Surv. Water-Res. Invest. Rep.* 80-96.
- Schwartz F. W., Crowe A. S., Hendry M. J. and Chorley D. W. (1987) A case study to assess the potential for saline soil development due to irrigation. *J. Hydrol.* **91**, 1–27.
- Scott G. R., Taylor R. B., Epis R. C. and Wobus R. A. (1978) *Geologic map of the Pueblo 1° × 2° quadrangle south-central Colorado*. U.S. Geol. Surv. Map I-1022, scale 1:250,000.
- Shannon S. S. Jr. (1978) *Uranium hydrogeochemical and stream sediment reconnaissance of the Pueblo NTMS quadrangle, Colorado*. Los Alamos National Laboratory. Informal Rept. LA-7341-MS, USDOE Rept. GJBX 135(78).
- Shannon S. S. Jr. (1979) *Uranium hydrogeochemical and stream sediment reconnaissance of the Lamar quadrangle, Colorado, including concentrations of forty-three additional elements*. Los Alamos National Laboratory. Informal Rept. LA-7342-MS, USDOE Rept. GJBX 64 (79).
- Sharps J. A. (1976) *Geologic map of the Lamar quadrangle, Colorado and Kansas*. U.S. Geol. Surv. Map I-944, scale 1:250,000.
- Taylor O. J. and Luckey R. R. (1974) Water-management studies of a stream-aquifer system, Arkansas River valley, Colorado. *Ground Water* **12**, 22–38.
- Tweto O. (1979) *Geologic map of Colorado*. U.S. Geol. Surv. Map, scale 1:500,000.
- U.S. Department of Commerce (1991) *National Climatic Data Center Climatological Data Annual Summary, Colorado*. Vol. 96, no. 13, ISSN 0145–0506.
- U.S. Department of Energy (1980) *Hydrogeochemical and stream sediment reconnaissance basic data for Dodge City NTMS quadrangle, Kansas*. Oak Ridge Gaseous Diffusion Plant Rept. K/UR-145 prepared for USDOE

- National Uranium Resource Evaluation Program, USDOE Rept. GJBX 77 (81).
- U.S. Environmental Protection Agency (1991) *National primary drinking water regulations for radionuclides, proposed rule*, June, 1991. Washington, D.C., Office of Ground Water and Drinking Water, EPA, Fact Sheet, Radionuclides in Drinking Water, 570/9-91-700.
- U.S. Environmental Protection Agency (1993) *Summary of EPA finalized national primary drinking water standards*. USEPA region VIII public information publication.
- U.S. Geological Survey (1991) Water Resources Data Colorado Water Year 1991. *U.S. Geol. Surv. Water-Data Rep.* CO-91-1.